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ION EXCHANGED, HIGH-STRENGTH GLASS COMPONENTS

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ABSTRACT: The tests were made with a photostructurable glass containing Li^+-, Na^+- and K^+-ions. The last step to make the microstructured glass components is an acid treatment which already enables them to a higher strength compared with window glass. For further increase of strength the ion exchange in melted, different nitrates was used. If in the layers near to the surface ions of a smaller radius are exchanged against such of a greater one, compressive stresses are generated in the ion exchanged layers. They compensate tensile stress during the application and can enlarge the bending strength of the glass components up to nearly 800 M Pa.

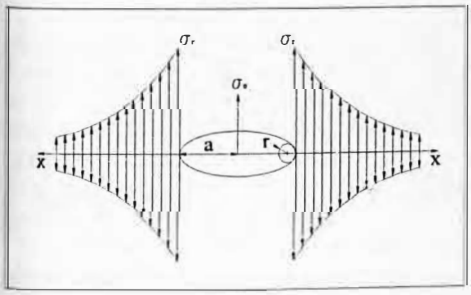
KEY WORDS: strength, ion exchange, microstructured glass, diffusion, fine annealing

1. INTRODUCTION

It is very well known that glass products are brittle and exhibit a low, scattering strength. The reason of this behaviour is the anion-cation-structure of anorganic-nonmetallic glasses which excludes a plastic deformation if stressed. Because any real glass product has micro cracks and flaws in its inner and near the surface an externally applicated tensile stress opens the cracks and creates stress maxima in its origin, see Fig. 1. Of course these maxima may be much greater compared with the measured average stress. They are the reason for glass breaking much earlier as expected. The real stress σ_r depends on the applicated average tensile stress σ_z, the half crack length a and the crack radius r in its origin, as given in Eq. (1):

$$\sigma_r = 2\,\sigma_z \sqrt{\frac{a}{r}} \qquad (1)$$

As larger r and as smaller a as smaller becomes σ_r. This fact is very well known and used in etching glass products to eliminate the surface cracks. An other possibility to improve the strength of glass products (not of the glass material itself) is the application of implemented in the surface layer compressive stress in order to close the cracks at least so long until the tensile stress exceeds the implemented compressive stress in the surface. This compressive pre-stress can be generated by thermal hardening or by ion exchange [1, 7, 8]. The produced stress profiles are drawn in Fig. 2.



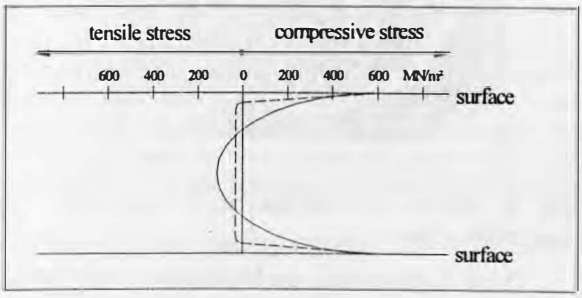


Fig. 1: Stress in dependence on the distance from the crack ends

Fig. 2: Stress profiles in a glass component after a thermal hardening (continuous line) or ion exchange (dotted line) [8]

2. GLASSPROBES

There are many progressions in the microstructuring of glasses [3, 4, 6]. But the application of the components frequently fails because of prejudices concerning the mechanical properties. Although it is very well known that glass fibers exhibit a much higher strength compared with specimens (DIN 52303) made from window glass, the applicator is not prepared to suppose this fact also for microstructured glass components. Therefore we have measured the strength of as received microstructured glass components and after an ion exchange without and with fine annealing the components during microstructuring. The method to do so was a modified photolithography of a masked UV-sensitive glass. Its composition is given in Tab. 1.

Tab. 1: Composition of the used UV-sensitive glass

main components		dopands	
oxide	mass-%	oxide	mass-%
SiO_2	74.29	Sb_2O_3	0.40
Al_2O_3	7.20	Ag_2O	0.12
Li_2O	11.61	SnO	0.07
Na_2O	2.74	CeO_2	0.03
K_2O	4.16		

The principle of microstructuring is the following: The melting regime enables to generate Ce^{3+} and Ag^+. The glass melt is pressed to form disks which are ground and polished. They are covered with a removable quartz glass mask. If applicating UV-radiation of the wavelength between 300 and 320 nm, in the exposed regions (holes in the mask) Ce^{3+} delivers a photoelectron to Ag^+, which becomes atomic silver. The silver atoms exist only in the exposured places. They are much more movable in the glass compared with silver ions. If heating the glass disk, e. g. up to 500 °C, the silver atoms diffuse and generate silver clusters. Possessing a diameter of nearly 7 nm, these clusters if being located in so called phase separation droplets act as crystal nuclei for $Li_2O \cdot SiO_2$ - crystals. During a following thermal treatment, e. g. at 570 °C, these crystals are growing. Their diameters between 100 nm and 1 µm depend on the chosen conditions of the thermal treatment, see [6]. Because of the very easy solubility of the $Li_2O \cdot SiO_2$-crystals in hydrofluoric acid it is now possible, to etch off the crystals and – in doing so – to microstructure the glass in the UV - exposured regions. Fig. 3 shows a microstructured glass component and Fig. 4 an array of 12 specimens for tests.

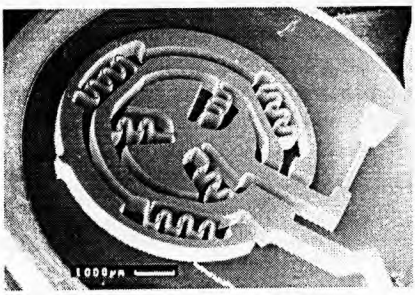


Fig. 3: Middle ear implant made from UV-stucturable glass

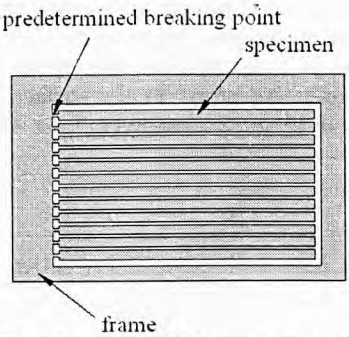


Fig. 4: Array of 12 specimens for bending test

These 12 specimens are broken out of the frame for bending tests in the as received state, or the complete frame including specimens is subjected to the ion exchange.

3. PROCEDURE OF ION EXCHANGE

The aim was to realize the ion exchange at temperatures below the strain-point (383 °C, [2]) of the glass in order to prevent a compressive stress annealing in the surface near layers by flowing during the ion exchange. The lowest reaction temperature is given by the melting point of the used salts ($LiNO_3$, $NaNO_3$ and KNO_3). As expected, the ion exchange in KNO_3 melts generates the highest compressive pre-stress. Therefore only these results will be reported. The reason for this effect is the great ion radius of K^+ ($r_{Li}+ = 78$ pm, $r_{Na}+ = 98$ pm, $r_K+ = 133$ pm). If replacing Li^+ or Na^+ by K^+, the later ion needs much more volume in the glass network compared with the other both, what generates compressive stress in the exchanged layers. It is necessary to find an optimum of temperature which is high enough for K^+-diffusion and low enough to avoid flowing. The procedure took place in a corrosion stable steel crucible positioned in a laboratory furnace. The micro structured glass specimen array was dipped into the melt and treated at temperatures between 345 up to 420 °C for ½ up to 48 hours. After each procedure the salt melt (300 g) was renewed. Two arrays of specimen were hanged up on a platinum frame in each exchange test. Following 24 specimen could be tested and used to calculate an average value of the bending strength at each testing point and of its scattering.

Specimen of a cross-section of nearly 1 x 1 mm^2 and a support distance of 2 cm were used for three-point-bending tests.

4. RESULTS

Because of the small dimensions of the specimen compared with the requirement of the DIN 52303 and because during making the specimen by photo structuring (the last step is as mentioned above an etching in hydrofluoric acid what avoids the generation of surface cracks and flaws) already the as received specimen have a bending strength of 340 ± 30 MPa. This is very high compared with commercially available glass tested by DIN (60 ... 80 MPa). That means, that – without post-treatment – microstructured glass components have a respectable strength.

The results after ion exchange for 30 min at different temperatures are given in Fig. 5.

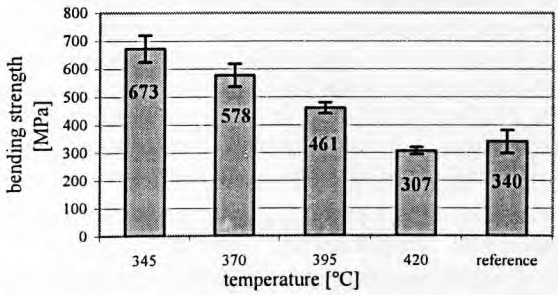


Fig. 5: Bending strength of specimen after an ion exchange in KNO_3-melts for 30 min at different temperatures

The strength is in maximum doubled compared with the untreated specimen. The effect diminishes with increasing temperature of ion exchange. A temperature of 345 °C is high enough for ion exchange by diffusion. The in-diffusing K^+-ions generate a compressive stress which compensates at the beginning of the bending test the tensile stress at the under site of the bar. This fact is the reason for the very high measured bending strength. If the exchange temperature is enhanced, the diffusion is more activated, but at the same time the glass starts to flow (annealing point = 383 °C). The as created stress anneales more and more. An elongation of the residence in the salt melt from ½ to 48 hours has a similar effect.

The evidence of the ion exchange as reason for the enhanced bending strength is given in Fig. 6.

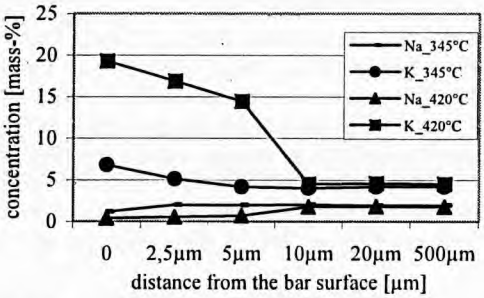


Fig. 6: K_2O- and Na_2O-concentrations in dependence on the distance from the specimen surface (0 = surface) after 30 min treatment in melted KNO_3

It is clearly visible that the K_2O-concentration at the surface of the glass specimens increases and the Na_2O-concentration decreases. The difference in concentration is caused by the not measurable Li_2O-profile. At 345 °C the diffusion depth is 5 µm, at 420 °C 10 µm. But all effects at 420 °C are annealed by flowing. Therefore the best ion exchange conditions in KNO_3-melts are 345 °C for 30 min. Additional tests were made by varying the microstructuring procedure. Between the thermal treatment for crystal growing and the etching we have inserted a so called fine cooling or annealing. It is a process commonly used for making stress free and more homogeneous, optical glass products. In our case we have expected more phase separation droplets and an influence on the silver-nucleation. The fine cooling (annealing) consists of the steps: Heating up to 480 °C with 8 K/min, 30 min residence time and again cooling to room temperature with 2 K/min. After the etching the ion exchange took place as described. The bending strength was very surprising, 777 ± 70 MPa, that means, once more an enhancement. The results in more details are given in [5].

5. SUMMARY

Microstructured glass components have originally a higher strength compared with common glass products. The reasons are the geometry of the test probes and the prevention of surface flaws by etching. An ion exchange in surface near layers, if ions with a greater radius replace such ones with smaller radius and, in doing so, create a compressive pre-stressed layer, causes an increase of bending strength to 673 ± 47 MPa. The best conditions for the ion exchange are 30 min at 345 °C in a KNO_3 melt. If a fine cooling (annealing) is inserted between the growth of Li_2O . SiO_2-crystals and their etching off, the strength of the test specimens once more increases to 777 ± 70 MPa.

6. REFERENCES

[1] BURGGRAF, A. J.: *The mechanical strength of alkali-alumosilicate glasses after ion exchange.* Philips Res. Rep. Suppl. 1966, No. 3, pp. 1 - 106

[2] HECHT-MIJIC, S.: Brechzahländerung durch Ionenaustausch in strukturierten Glasbauteilen. Doctor-thesis, TU Ilmenau, 2003

[3] HESSE, A.: Modifizierung von fotostrukturierbarem Glas durch partielle Kristallisation. Diploma-thesis, TU Ilmenau, 2004

[4] LUDWIG, Y.: *Parameteruntersuchungen zum Ätzprozess von fotostrukturierbarem Glas.* Project-thesis, TU Ilmenau, 2003

[5] LUDWIG, Y.: *Modifizierung von fotostrukturiertem Glas durch Ionenaustausch.* Diploma-thesis, TU Ilmenau, 2004

[6] MROTZEK, S.: *Kristallisation eines UV-strukturierbaren Glases im System Li_2O-Al_2O_3-SiO_2.* Doctor-thesis, TU Ilmenau, 2005

[7] SCHOLZE, H.: *Glas – Natur. Struktur und Eigenschaften.* Springer Verlag, Berlin, 1977

[8] SPAUSZUS, S.: *Werkstoffkunde Glas.* VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974